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The Interaction of HCN(DCN) with Si(111)-7x7 Studied  
with HREELS, UPS and XPS

by

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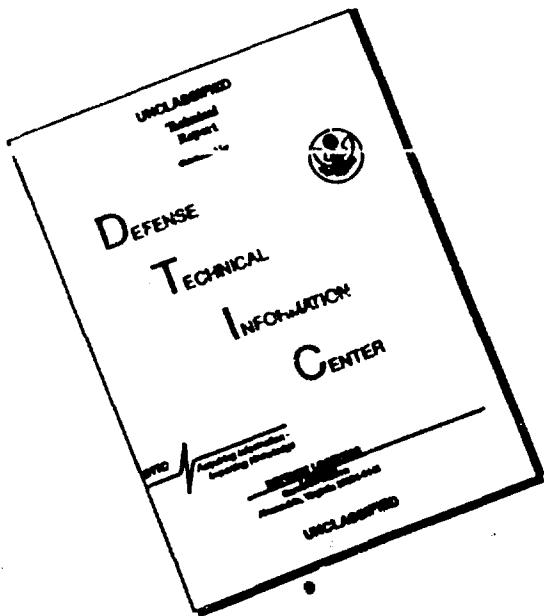
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## Abstract

The interaction of HCN (DCN) with Si(111)-7x7 was studied with high resolution electron energy loss spectroscopy (HREELS), ultra-violet photo-electron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). HCN (DCN) formed dimers and/or polymers on the surface at 100 K with higher dosages ( $D>4$  L). Above 200 K, CN radicals in an end-on adsorption geometry were identified as the major species which survived up to 600 K on the surface. This observation was different from that with HCN (DCN) on Si(100)-2x1, where the relative concentration of the HCNH species was higher. The observed difference in the behavior of HCN (DCN) on Si(111)-7x7 and Si(100)-2x1 could be ascribed to the different topologies of the two surfaces.

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## **Introduction**

The behavior of the CN-containing species on metal surfaces has been studied extensively; e.g., HCN interacted differently with Pt(111)<sup>1,2</sup> and Pd(111)<sup>3</sup>, and the predosing of O<sub>2</sub> on Cu(111)<sup>4,5</sup> was found to cause the reorientation of the CN radical on the Cu surface. On the other hand, very little has been reported on the reactions between these compounds and semiconductor surfaces. In the first part of this series of studies<sup>6</sup>, we have reported the adsorption and the thermal decomposition of HCN (DCN) on Si(100)-2x1. We have found that at higher dosages ( $D > 4 \text{ L}$ ) and lower surface temperatures ( $T_s = 100 \text{ K}$ ), HCN formed dimers and/or polymers on Si(100). After the sample was warmed to 220 K, both CN and HCNH species were identified on the surface. Above 680 K, the C≡N stretching vibrational mode disappeared in HREELS, indicating the breaking of the CN bond. After the surface was annealed to  $T_s > 820 \text{ K}$ , the H species began to desorb from the surface following the breaking of the C-H and N-H bonds, and C and N species remained on the surface forming carbide and nitride, respectively. In this work we investigated the interaction of HCN (DCN) with Si(111)-7x7; the new results are compared with those obtained from HCN (DCN) on Si(100)-2x1.

## **Experimental**

The experiments were carried out in the same system as reported in the first part of the work<sup>6</sup>. The Si(111) single crystals from Virginia Semiconductor Inc. were cut into 1.5 cm x 1.0 cm samples. They were cleaned with a 5% HF solution before being introduced into the UHV system and were further cleaned by repeated annealing at  $T_s > 1500 \text{ K}$  in vacuum until no C, N and O impurities could be detected by AES, XPS and HREELS. The surfaces prepared in this way showed a sharp 7x7 LEED pattern, indicating a well-characterized surface to start with. Although the same straight-through electron beam was used in HREELS measurements, the beam

scattered from Si(111)-7x7 was a few times weaker than that scattered from Si(100)-2x1 as measured by the elastic peak heights. HCN (DCN) samples were prepared by the acidification of NaCN as described in ref. (6).

## Results

### A. HREELS:

Figure 1 shows the HREELS of 4 L HCN (a) and DCN (b) on Si(111)-7x7 taken at specular and 11° off-specular angles, respectively. After 4 L HCN (DCN) was dosed on the surface at 100 K, HREELS produced peaks at 83, 105 (85), 205 (165 shoulder), 265 (235-265) and 398 (320) meV. By comparing with the IR results of the gaseous HCN<sup>7</sup> and HREELS results of HCN adsorbed on Si(100)-2x1, we attributed these peaks to the vibrational modes for monomeric, dimeric and/or polymeric HCN as listed in Table 1. The intense peaks at 105 (85) and their overtones at 205 (165), 265 (235) and 398 (320) meV dominated the HREEL spectra, indicating the formation of the HCN (DCN) dimer and/or polymers on the surface under the indicated experimental conditions. On the other hand, the peak at 83 meV for HCN on Si(111) was due to the deformational vibration of the monomeric HCN Si-CHN stretching mode and possibly second harmonic of the 28 meV mode. The latter peak due to the intermolecular torsional vibration<sup>4,6</sup> could be clearly resolved from the elastic peak with the improved resolution as also shown in Figure 1a. Two small humps at 235 and 325 meV were due to a trace of DCN on the surface in the case of HCN on Si(111), while the peaks at 112, 398, 420 meV and part of the 265 meV peak in the DCN HREELS were due to the presence of a small amount of HCN.

The corresponding HREEL spectra taken in the off-specular angle show that the 83, 105 (85) and 265 meV peaks are mainly due to the dipole scattering, while the other peaks are due to impact scattering. Interestingly, the 265 meV peak in the DCN HREELS is too strong to be attributed purely to the HCN contamination, since the

relative intensities of the 112, 398 and 420 meV peaks due to HCN species are rather weak. Furthermore, in the off-specular spectrum, the 265 meV peak intensity was attenuated more than that of the 235 meV peak, the corresponding C≡N stretching mode for DCN species. These observations suggest the presence of another species, the CN radical. The CN radical was also observed in HCN on Si(100) but to a lesser extent and its formation became more obvious when the surface was annealed to higher temperatures.

After the sample was warmed to 220 K, the 235 meV peak in DCN HREELS (Figure 2b) vanished, while the relative intensity of the 265 meV peak increased. These changes clearly indicated the increased cracking of the D-C bond and the formation of the CN radicals on the surface. Because of the absence of an obvious Si-D stretching mode at ~200 meV, the other product was presumably the DCND species, as evidenced by the two noticeable humps at 312 and 342 meV<sup>6</sup>. In the corresponding HCN HREELS (Figure 2a), these two modes appeared at 375 and 425 meV, in addition to a peak at 162 meV. These three peaks agree reasonably with a quantum chemical calculation by Melius as discussed earlier<sup>6</sup>, and they could be attributed to the C-H, N-H and HC=NH stretching vibration frequencies of the HCNH species on Si substrates. For HCN on Si(100), these three peaks, which appeared at 160, 368 and 418 meV, respectively, were more intense as compared to those derived from HCN on Si(111). Here the observed weak HCNH features are probably due to a partial desorption of this species, which will be discussed further below. The remaining peak at 85 meV and the shoulder at 117 meV were mainly due to the surface-adsorbate stretching vibrations, and the combination of these modes is likely responsible for the hump at 200 meV in the HCN spectra (Figure 2a). Finally, the significant attenuation of the 105 (85) meV peak in the 220 K HCN (DCN) spectrum was caused mainly by the appreciable desorption of the adsorbate, as clearly indicated in the XPS results and also discussed in detail for HCN on Si(100)-2x1.

Further annealing the samples to 600 K caused no obvious change in the HCN (DCN) HREELS except the attenuation of all peak intensities due to the further desorption of the adsorbates. In addition, the decrease of the 162, 375 and 425 meV (see Fig. 2a) also suggests a partial dissociation of the HCNH species, which is more clearly observed in the corresponding UPS and XPS results. At 800 K, the CN bond breaking occurred as was evidenced by the disappearance of the 265 meV and the shift of the 85 and 117 meV peaks to 100 and 125 meV, respectively, with their relative peak intensity changed. The latter two peaks are due to the Si-C and Si-N stretching vibrations, which were also observed in the case of  $\text{CH}_3\text{N}_2\text{H}_3$  on Si(111)-7x7 after annealing the sample at  $T_s > 1000$  K<sup>8</sup>.

#### B. UPS

Figure 3 summarizes the thermal effect on the He(II) UPS of 4 L HCN dosed Si(111). All curves are differential spectra, obtained by subtracting the spectra taken from the dosed and annealed samples from that taken from the clean surface. When 4 L HCN was dosed on the surface at 100 K, UPS presented peaks at 13.4, 7.6 and 5.2 eV below  $E_F$ . By analogy to the corresponding UPS results of HCN in the gas phase and adsorbed on Pd(111)<sup>3</sup> and Si(100)<sup>6</sup>, the former two peaks could be assigned to the 4  $\sigma$  and 1  $\pi$  plus 5  $\sigma$  molecular orbitals in HCN, respectively. In contrast, the weak 5.2 eV peak is somewhat difficult to assign. We tentatively attribute this peak to a small amount of C=N containing (HC=N, HC=NH and possibly some C=NH) species, presumably due to the N lone-electron pairs, for the following reasons: 1) The characteristic C=N peaks (160 and 200 meV) in HREELS were attenuated at 220 K and vanished at 600 K, so was the 5.2 eV peak in UPS; 2) For HCN on Si(100), the 5.2 eV peak was more intense, and so were the 160 and 200 meV peaks in HREELS at 100 and 220 K. This is because the concentration of the C=N containing species is higher on Si(100) than on Si(111); 3) The 5.2 eV peak was absent in the UPS of

$C_2N_2$  on both Si(111) and Si(100) at 100 to 800 K, according to our recent study; this would rule out the possibility that the 5.2 eV peak originated from the CN radicals. This was also indicated in the HREELS results of HCN on Si(111), that the 265 meV peak due to the CN radical was fairly strong at 600 K, while the 5.2 eV peak in UPS virtually vanished at the same temperature.

As the sample was warmed to 220 K, the 7.6 and 5.2 eV peaks were substantially attenuated and shifted to 6.3 and 4.8 eV, respectively. Meanwhile, the 13.4 eV peak virtually disappeared. The peak intensity change at this temperature was obviously the reflection of the partial desorption of the adsorbate, while the shift of the 7.5 eV peak to 6.3 eV resulted mainly from the dissociation of HCN. At this temperature, the dominant adsorbates are CN and some HCNH as was clearly evident in the HREEL spectra presented earlier. When  $C_2N_2$  dissociatively adsorbed on Pd(111), the CN radicals also produced a peak at 6 eV in UPS. On the other hand, the reduced adsorbate-adsorbate interaction after the desorption of the overlayer HCN and a stronger screening in the final state are likely responsible for the 5.2 eV and partially the 7.5 eV peak shift. As the surface was annealed at 600 K, the UP spectrum was dominated by a single peak at 6 eV, which was also slightly enhanced (~5% in peak area) due to the decomposition of the HCNH species to produce more CN radicals. This observation is different from that for HCN on Si(100), where the peak area increase by more than 30% was observed due to the reorientation of the CN radicals on Si(100). At 800 K, the 6 eV peak was attenuated, broadened and shifted to 6.5 eV because of the desorption and dissociation of the CN radicals as well as the formation of Si-C and Si-N bonds. Finally, the absence of the 12 eV peak above 220 K suggested a smaller concentration of the C-H and N-H containing species on Si(111). For HCN on Si(100), the 12 eV peak in UPS persisted up to 620 K and the corresponding C-H and N-H stretching modes in HREELS were also more intense.

### C. XPS

Figs. 4a and 4b illustrate the thermal effects on N<sub>1S</sub> and C<sub>1S</sub> XPS for a 4 L HCN dosed Si(111) sample. When HCN was dosed on Si(111) at 100 K, peaks at 400.5 and 287.5 eV with FWHM's of about 1.6 eV were noted for N<sub>1S</sub> and C<sub>1S</sub> photoelectrons, respectively. These two peaks are essentially the same as those observed for HCN on Si(100) and are due to the dimeric and/or polymeric HCN adsorbed on the surface. As this 4 L HCN dosed sample was warmed to 220 K, a reduction of signal intensity by ~75% for both N<sub>1S</sub> and C<sub>1S</sub> XPS was noted, indicating a substantial desorption of the adsorbate. Meanwhile, the N<sub>1S</sub> and C<sub>1S</sub> peaks broadened considerably and shifted to 398.9 and 286.0 eV, respectively. At this temperature, there are at least two adspecies, CN and HCNH, on the surface as identified by the corresponding HREELS and UPS. Annealing the sample at 500 to 600 K narrowed the N<sub>1S</sub> and C<sub>1S</sub> peaks and shifted peak centers further to 398.3 and 285.5 eV, because CN radical is the dominant adspecies. On the other hand, the 600 K C<sub>1S</sub> XPS having some contribution from the lower energy component at 283.3 eV, originated from the Si carbide, suggests a partial breaking of the CN bond. The breaking of the CN bond continued at 700 K and virtually completed at 800 K as indicated by the growth of the 283.3 eV C<sub>1S</sub> peak at 700 K, which dominated the spectrum at 800 K. Meanwhile, the N<sub>1S</sub> peak shifted to 397.7 and 397.5 eV at 700 and 800 K, respectively. Since the values of 397.5 and 283.3 eV for N<sub>1S</sub> and C<sub>1S</sub> photoelectrons are very close to those obtained from the Si nitride<sup>10</sup> and Si carbide<sup>11</sup> samples, the 800 K XP spectra indicate the dissociation of the CN bond and the formation of the Si-N and Si-C bonds, in consistence with our HREELS and UPS results.

### Discussion

The interaction of HCN (DCN) with Si(100)-2x1<sup>6</sup> and Si(111)-7x7 has been studied with HREELS, UPS and XPS. At higher dosages ( $D > 4$  L) and  $T_s = 100$  K,

HCN formed dimers and/or polymers on the surfaces, which dominated the LEEL as well as the UP spectra. When the samples were warmed to 220 K, both CN and HCNH species were identified on these surfaces. CN was the major species on Si(111), whereas the relative concentration of HCNH was higher on Si(100) than on Si(111). These differences, clearly shown in both HREELS (note the different scale of the 260 meV peak) and UPS (the absence of 12 eV peak for HCN on Si(111) at above 220 K), may be attributed to the different topologies of the two surfaces.

For a reconstructed Si(100)-2x1 surface, dimers are formed between the two adjacent surface Si atoms. As a result, one of the two dangling bonds on each Si atom is involved in the dimer formation, while the other remains unsaturated. The distance between the dimer Si atoms is about 2.3 Å, thus a CN containing species could form either an end-on or a di- $\sigma$  side-on adsorption geometry on the surface. Furthermore, a dimeric HCN can also be formed on Si(100)-2x1. One example is shown in Fig. 5a, in which the two C atoms interact with the two dangling bonds of the Si dimer atoms. Considering the tilt of the Si dangling bond from the surface normal ( $\sim 30^\circ$ ), one can estimate that the distance between the N atom in one HCN and the H atom in the other matches well with the value of 2.02 Å, the H-bond distance reported for crystal HCN. After the breaking of the H bond, HCNH species could bond to the surface with both C and N atoms, while the CN radical remains bonded to the Si dangling bond as shown in Fig. 5b. Both HCNH and CN species were identified in the HREELS for HCN on Si(100) at 220 K<sup>6</sup>. At this temperature, breaking, or more likely, partial breaking of the Si dimer bond may also take place and the energy loss can be compensated by the partial formation of a stronger SiN bond. The experiment results suggest that as the surface was annealed at 560 K, some of the CN radicals appeared to reorient themselves from the end-on to a side-on adsorption geometry. Such a reorientation of the CN radical could occur either by breaking the Si dimer bond if there is no other CN containing species adsorbed on the same Si dimer unit or

through the formation of a SiN bond between the N atom in the CN radical and the Si atom in the adjacent Si dimer if there is no site available in the same Si dimer unit (See Fig. 5c). *Although the distance between the Si atoms of the two adjacent dimers is about 5.4 Å, (a distance too large for the Si-CN-Si formation), this distance may be reduced after the breaking of the Si dimer bond and the formation of Si-HCNH-Si species.* Thus, the formation of Si-CN-Si becomes feasible, as shown in Fig. 5c. Such a structure requires the reduction of the distance between the Si atoms to about 3.8 Å, the value for the adjacent Si distance on an unreconstructed Si(100) surface. Furthermore, because the bond lengths for C=N, Si-C and Si-N are about 1.3, 1.8 and 1.6 Å, respectively, the angles for CSiSi and NSiSi would be about 45° in the proposed model.

The HCNH species could also dissociate into either HCN or HNC species with the H atom occupying the unsaturated Si dangling bond as shown in Fig. 5d. In fact, the latter two species were observed in the corresponding 560 and 620 K HREEL spectra<sup>6</sup>.

For the reconstructed Si(111)-7x7 surface, the distance between the dangling bonds (~5 Å between an adatom and its adjacent rest atom) is too large for the formation of a SiCNSi, but it is a reasonable distance for the formation of a Si-(HCN)<sub>2</sub>-Si species. The latter, shown in Fig. 6a, requires only a tilting of the Si dangling bonds by <10°, if a value of 2.0 Å is taken for the hydrogen-bond length. After the breaking of the HCN dimer, a σ-bond could be formed between the C atom in CN and the Si dangling bond with the CN radical standing up on the surface as shown in Fig. 6b. As to the HCNH species, it would probably adsorb on the surface with a σ-bond in a tilted end-on geometry (see Fig. 6b). In this case, some HCNH species may desorb from the surface, or more likely, decompose into SiH + HCN(g), due to the lack of favorable surface sites for HCNH to form a side-on adsorption geometry on the surface. This is evident in the HREELS with the three weaker peaks at 162, 375 and

425 meV due to the HC=NH, C-H and N-H stretching modes, respectively, for HCN on Si(111)-7x7 than on Si(100)-2x1 at temperatures above 220 K. On the other hand, one strong peak at 265 meV from the CN radicals persisted up to 600 K with no evidence of reorientation of the CN species for HCN on Si(111)-7x7.

Previously, it was found that Si back bonds broke when an NH<sub>3</sub>-dosed Si(111)-7x7 sample was annealed at temperatures above 600 K<sup>9</sup>. Such a process appeared to occur also in the present study, because the 800 K HREEL spectrum was dominated by the Si-C and Si-N stretching modes at 100 and 125 meV, respectively (see Fig. 2). The formation of the SiC and SiN species would require the breaking of the Si-Si back-bonds.

### Conclusion

The interaction of HCN (DCN) with Si(111)-7x7 was studied in the temperature range of 100 to 820 K. At T<sub>S</sub> = 100 K and higher dosages (D > 4 L), HCN (DCN) formed dimers and/or polymers on the surface. Warming the sample to 220 K caused the desorption and the dissociation of the HCN species; both CN and HCNH were identified on the surface. The CN radical was the major species present in an end-on adsorption geometry, which persisted up to 600 K as indicated by the strong 265 meV peak in HREELS. In contrast, for HCN adsorbed on Si(100)-2x1, the relative concentration of the HCNH species was larger and some of the CN radicals reoriented on the surface at 560 K. The observed difference between HCN interaction with Si(111)-7x7 and with Si(100)-2x1 could be rationalized by the different topologies of the two surfaces.

When the sample was annealed to higher temperatures, the dissociation of the CN, CH and NH bonds occurred, followed by the desorption of the H species. Above 820 K, only C and N species remained on the Si(111) surface.

## Acknowledgments

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**Table I.** Vibrational Frequencies Observed for HCN (DCN) on Si(111)-7x7 at Different Temperatures<sup>a</sup>

	100 K	220 K	600 K	800 K
$\nu_{\text{aNH}}$	420(340)	~425 (~340)	~425(~340)	
$\nu_{\text{sNH}}$	398(320)			
$\nu_{\text{CH}}$		~375 (~320)	~375(~320)	
$\nu_{\text{CN}}$	260(235)	256(260)		
$\nu_{\text{Si-H}}$			260 (200)	280(200)
$2\delta$	210(160)			
$\nu_{\text{C=N}}$		~162		
$\delta_{(\text{HCN})n}$	105(85)			
$\delta_{\text{HCN}}$	80			
$\nu_{\text{Si-C}}$		85(87)	85(85)	100(~100?)
$\nu_{\text{Si-N}}$		~110 (~112)	~115(~115)	~125(125)
$\tau_{(\text{HCN})n}$	28			

a. The surface was annealed to the indicated temperature and cooled down to 100 K for the sequential HREELS measurements.

**Table II.** Known Vibrational Frequencies of Some CN-containing Species

Mode	HNC(DNC) <sup>a</sup> (gas)	HCNH cal. <sup>b</sup>	HCNH (DCND) on Si(100) <sup>c</sup>	C <sub>2</sub> N <sub>2</sub> <sup>d</sup>
$\nu_{\text{NH}}$	447(342)	407	425(310)	
$\nu_{\text{CH}}$		364	368(~310)	
$\nu_{\text{CN}}$	252(241)	190	160(124)	289 268
$\nu_{\text{CC}}$				105
$\delta_{\text{HNC}}$	65(50)			
$\delta_{\text{NH}}$		148		
$\delta_{\text{CH}}$		123		
$\delta_{\text{HCNH}}$		115		$\delta_a$ 62
				$\delta_a$ 29

a. Ref. 12; b. Ref. 13; c. Ref. 6; d. Ref. 14

## **Figures Captions**

- Figure 1.** The HREELS of 4 L HCN (a) and DCN (b) on Si(111)-7x7 at 100 K taken in the specular (1) and 11° off-specular (2) angles, respectively.
- Figure 2.** Thermal effects on the HREELS of 4 L (a) HCN and (b) DCN dosed Si(111)-7x7. All spectra were recorded by annealing the sample at the indicated temperatures for 1 minute and then cooling to 100 K for 5 minutes.
- Figure 3.** Thermal effects on the He(II) UPS of 4 L HCN dosed Si(111)-7x7. All curves are the differential spectra, obtained by subtracting the spectra taken from the dosed and annealed sample from that taken from the clean surface.
- Figure 4.** N<sub>1S</sub> (a) and C<sub>1S</sub> (b) XPS taken from a 4 L HCN dosed Si(111) at 100 K and after annealing at the indicated temperatures.
- Figure 5.** The proposed model for the adsorption geometry of HCN on Si(100)-2x1 at the indicated temperatures.
- Figure 6.** The proposed model for the adsorption geometry of HCN on Si(111)-7x7 at the indicated temperatures.

Fig. 1a.

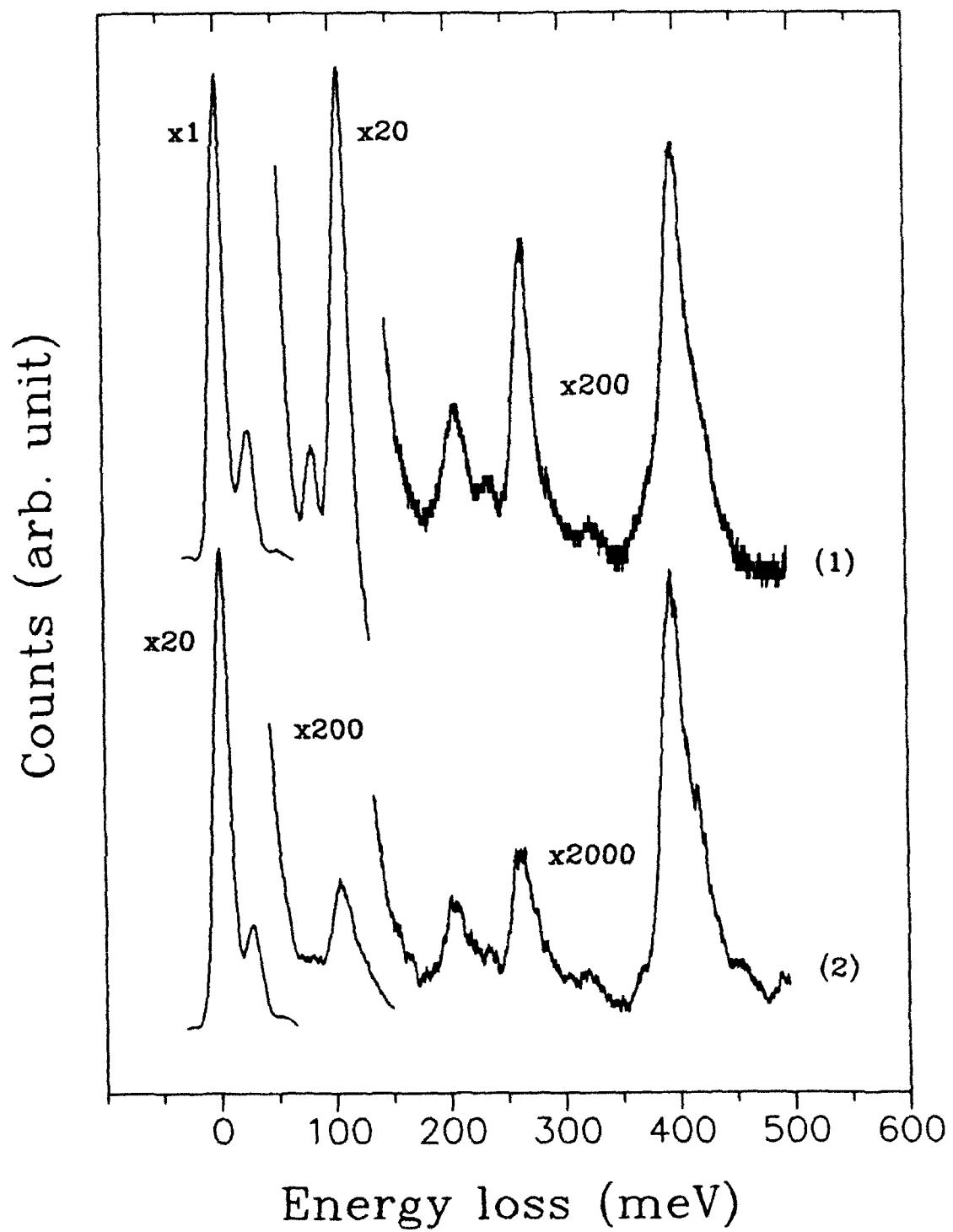


Fig. 1b.

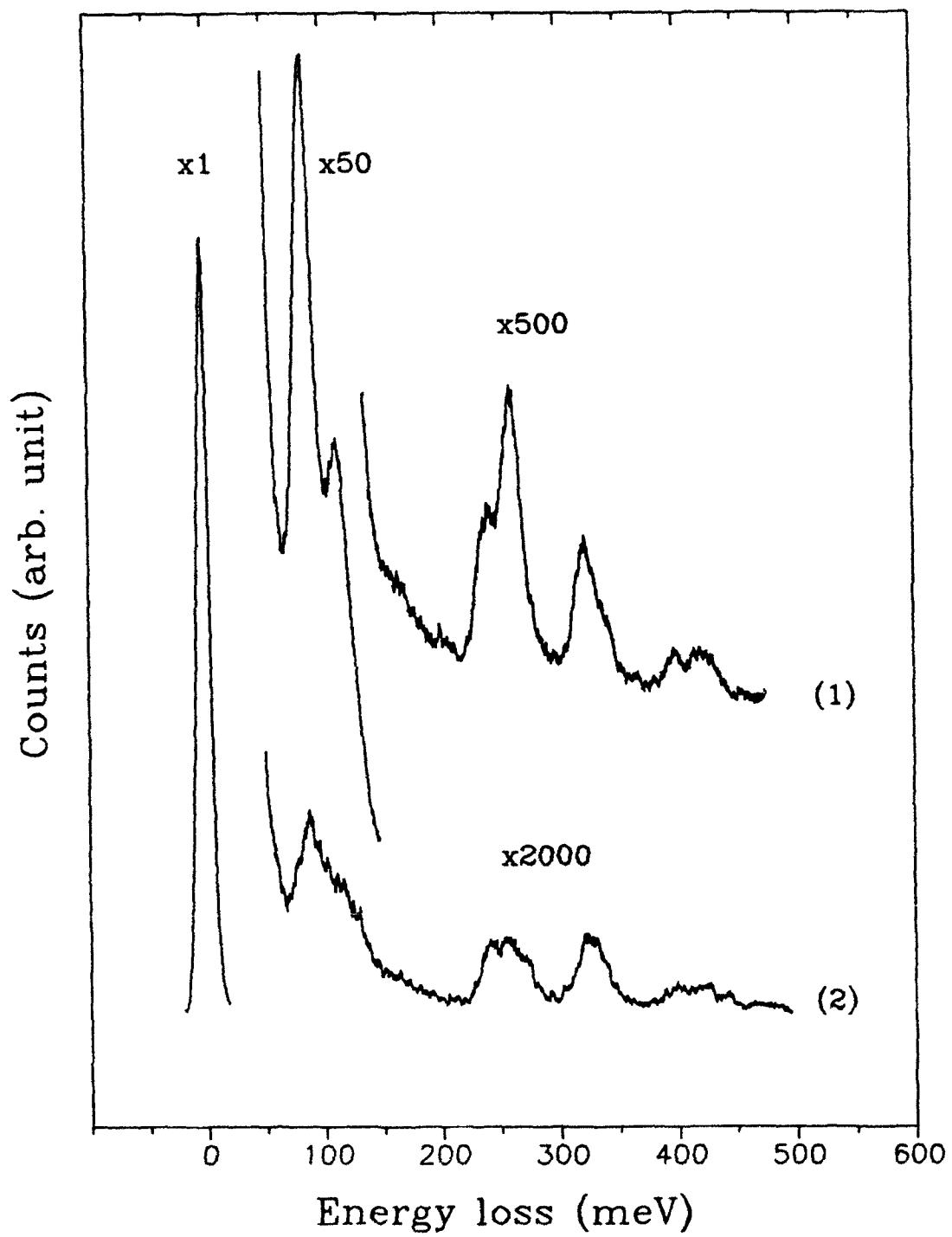


Fig. 2a.

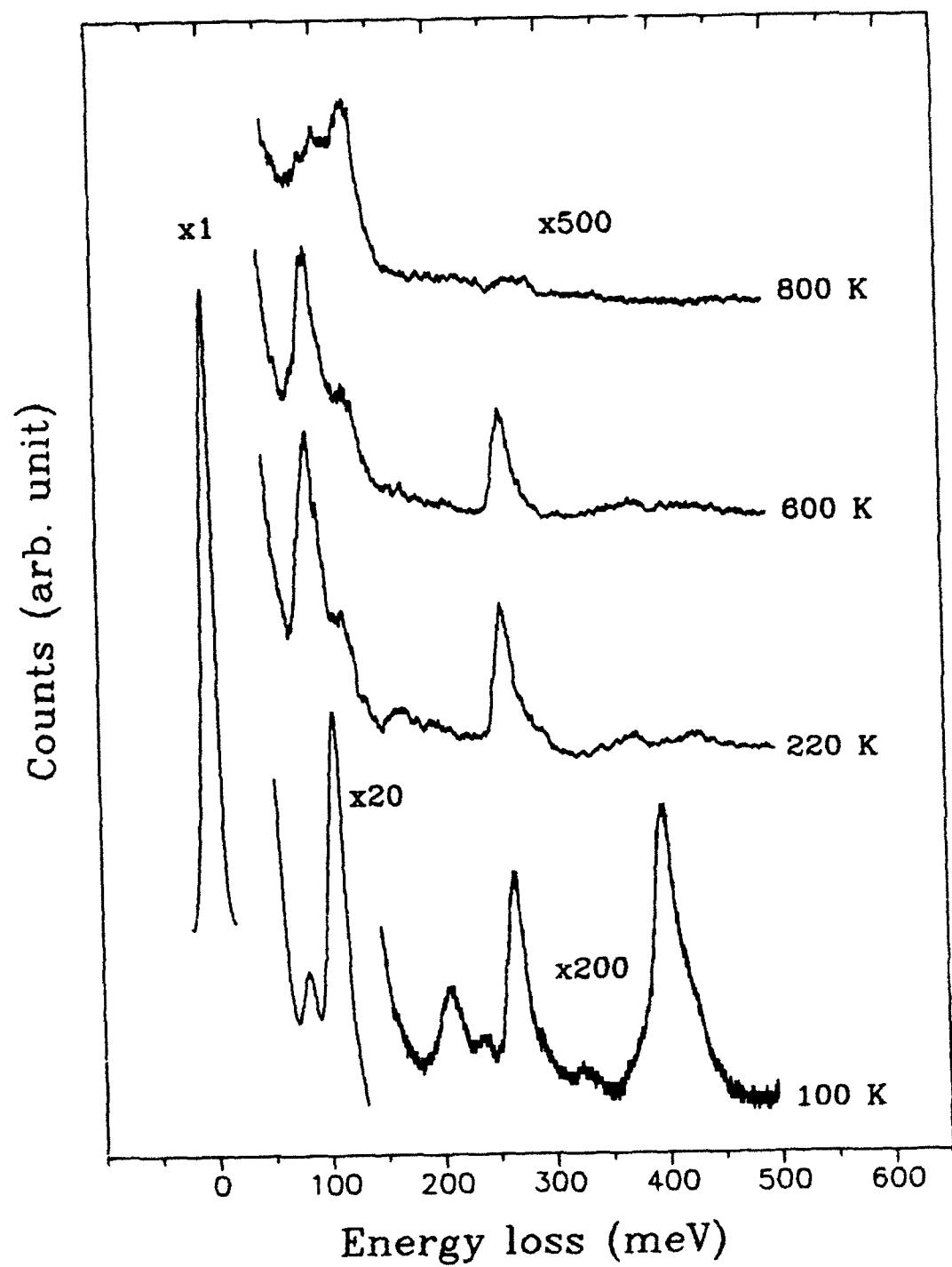


Fig. 2b.

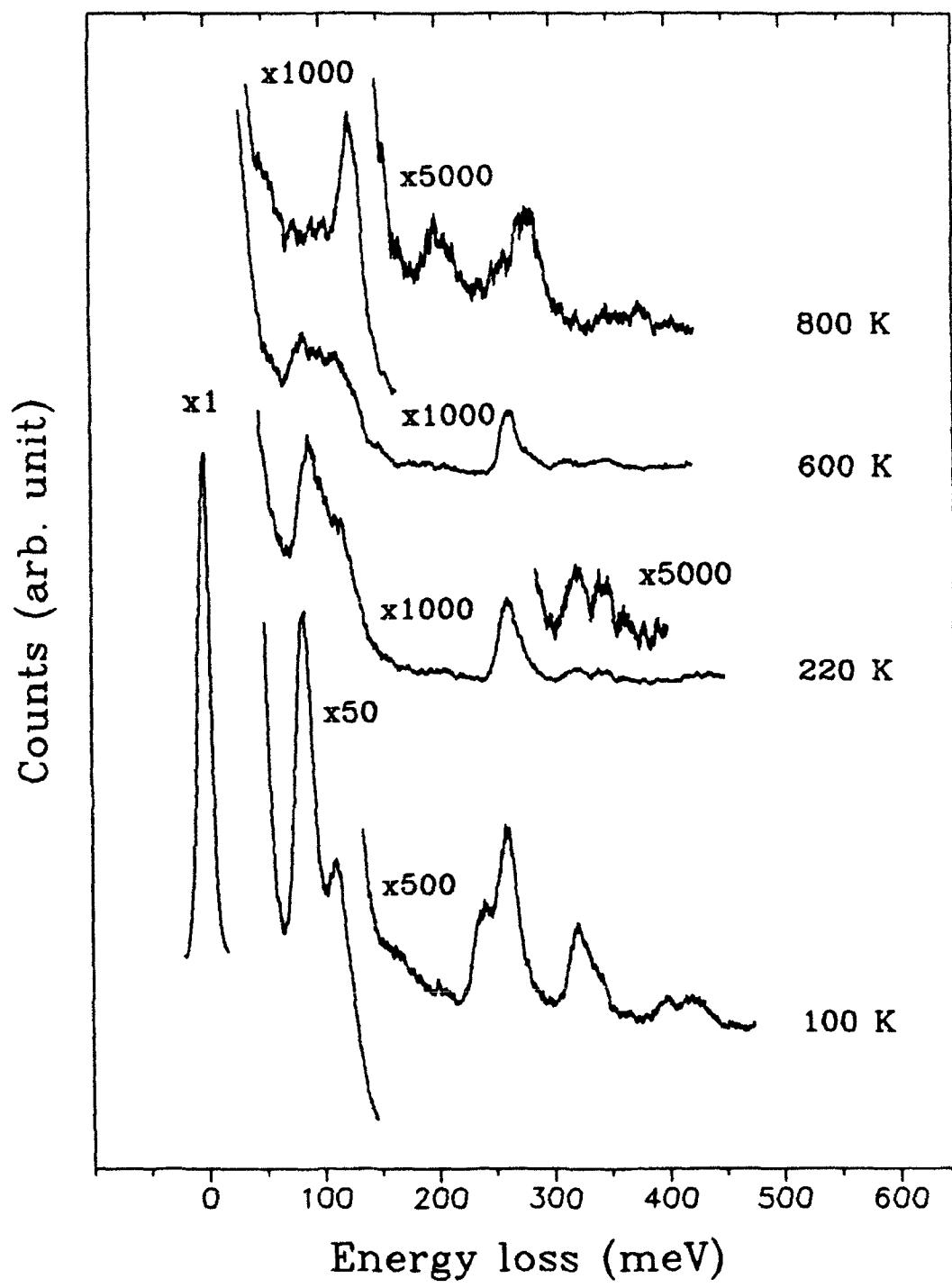


Fig. 3.

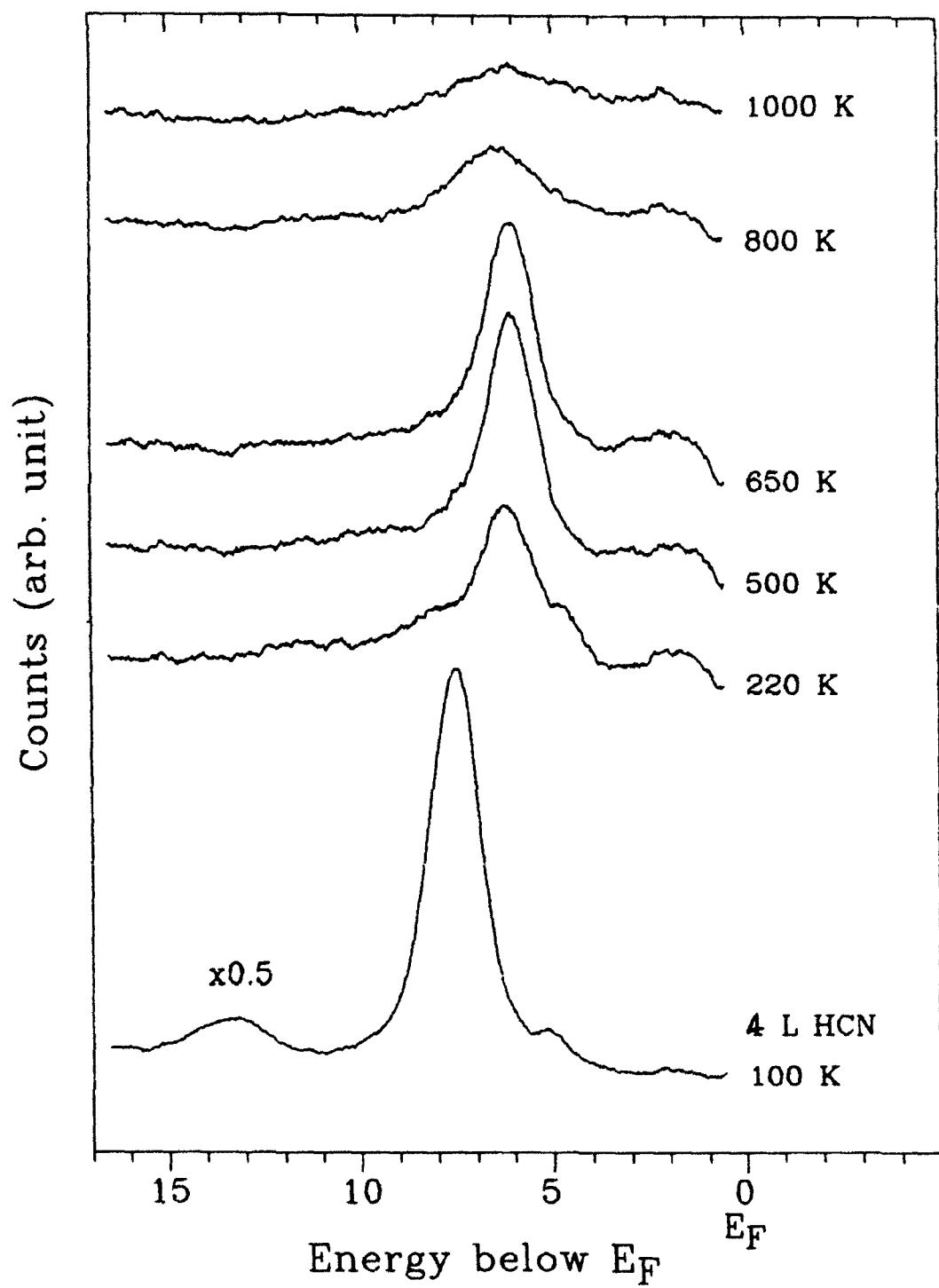


Fig. 4a.

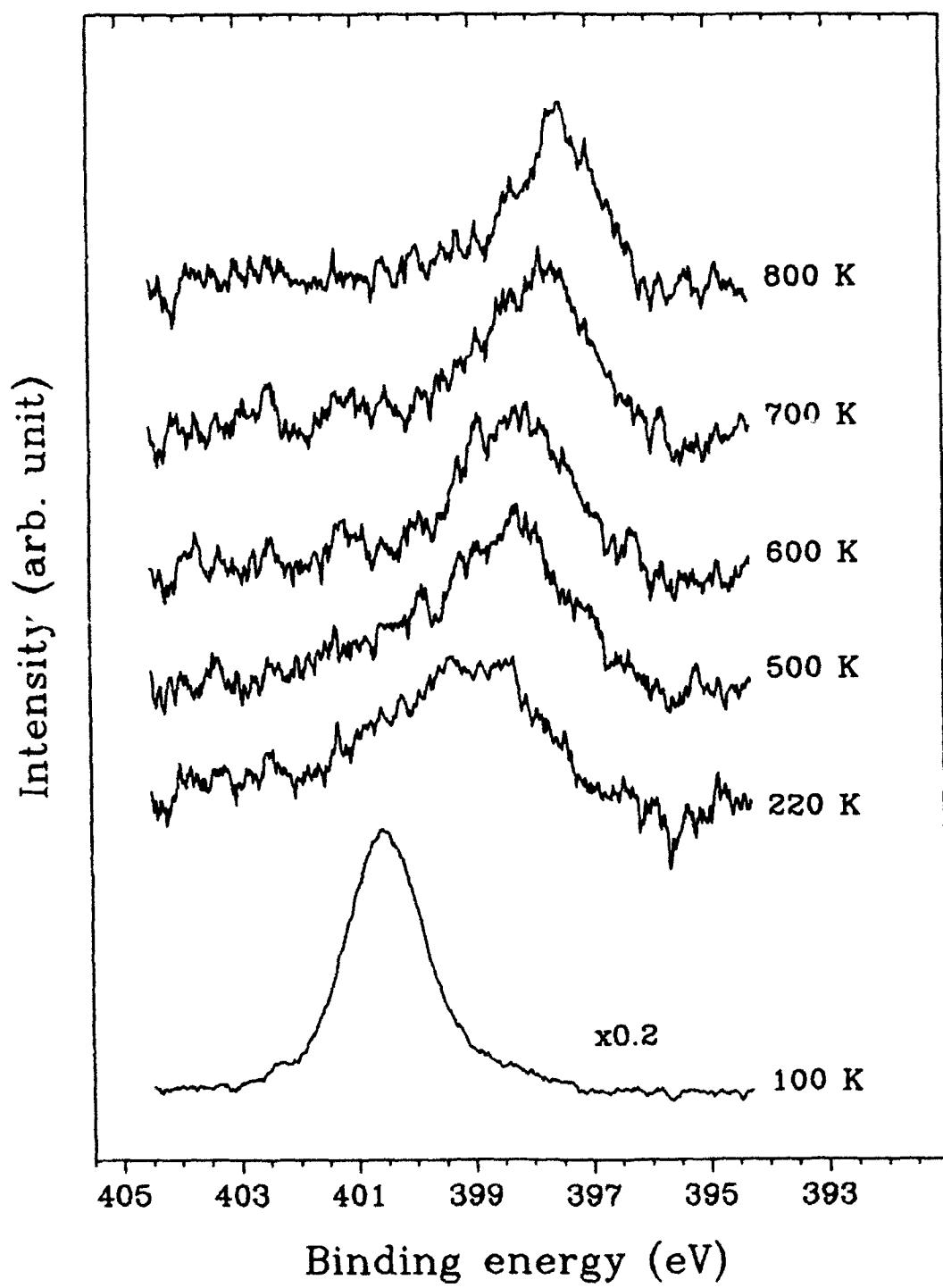


Fig. 4 b.

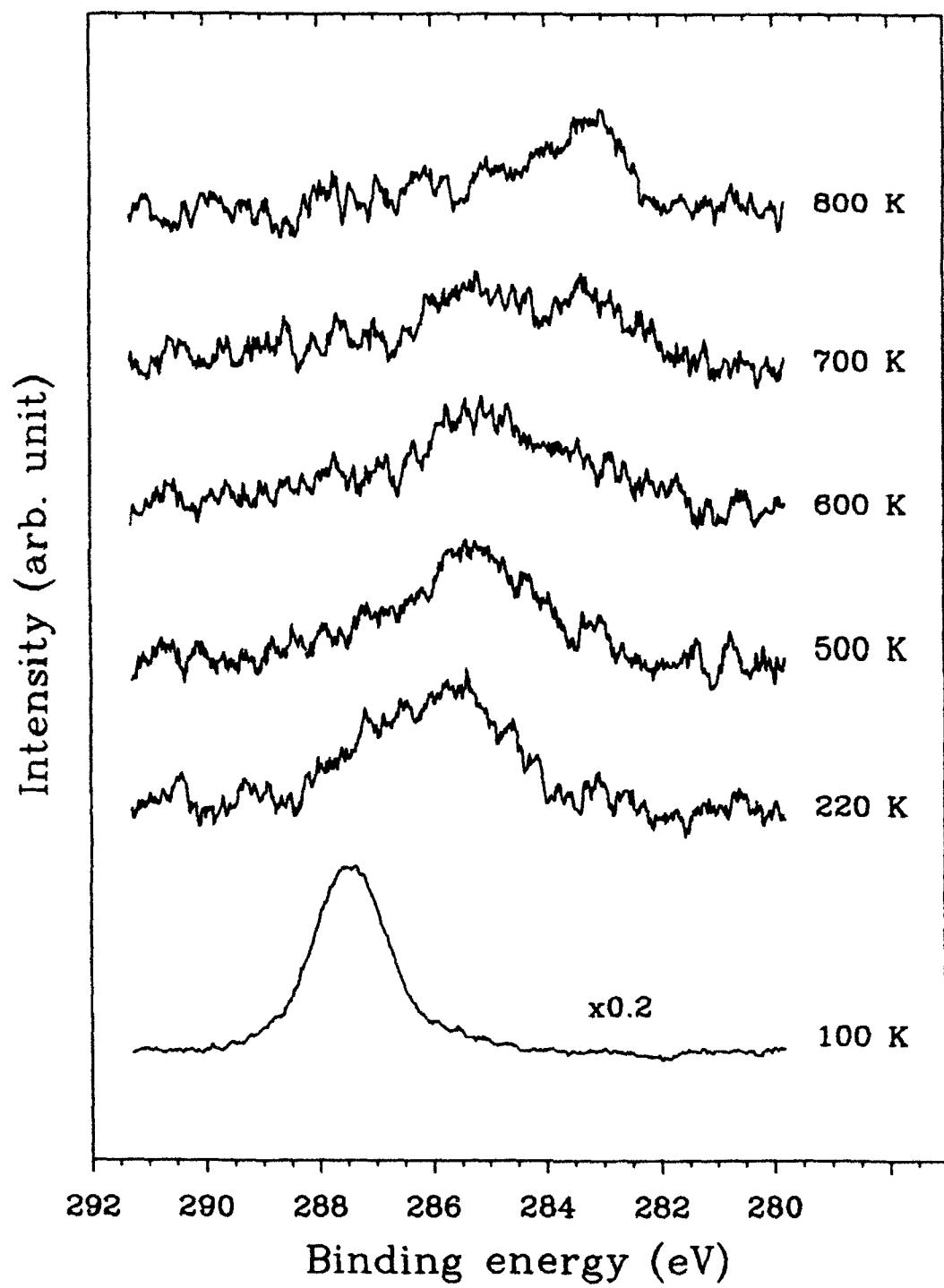


Fig. 5

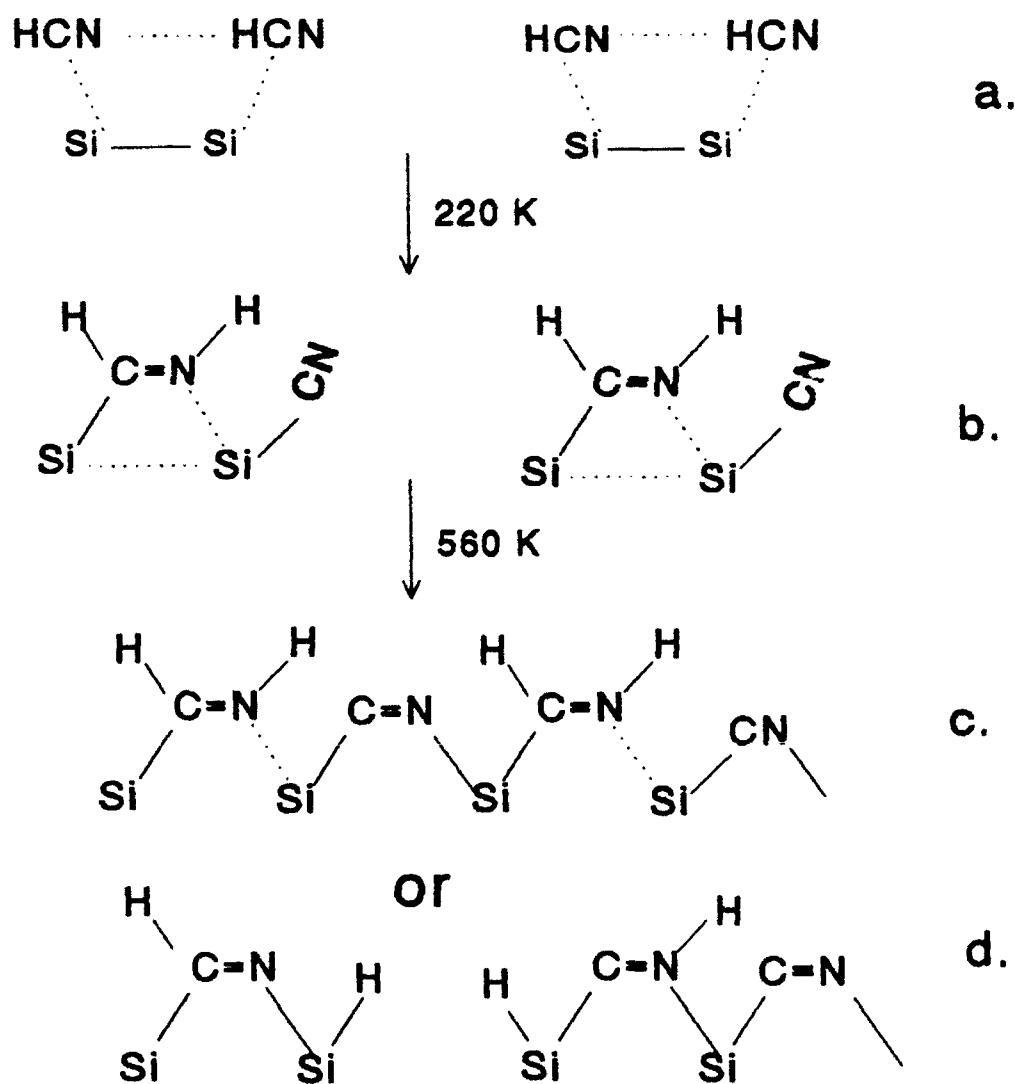


Fig. 6.

